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# 婆婆针的化学成分

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**摘要**　婆婆针(*Bidens bipinnata* Linn.)是具有清热解毒功效的民间药用植物.从婆婆针的地上部分分离鉴定了 3 个苯丙素甙类化合物, 4-O-(6″-O-对-香豆酰基-β-D-吡喃葡萄糖)-对-香豆酸(1),4-O-(2″-O-乙酰基-6″-O-对-香豆酰基-β-D-吡喃葡萄糖)-对-香豆酸 (2) 及 4-O-(2″,4″-O-二乙酰基-6″-O-对-香豆酰基-β-D-吡喃葡萄糖)-对-香豆酸 (3), 其中(3)为一新化合物.同时还得到 5 个已知化合物, (顺)-6-O-(4″,6″-二乙酰基-β-D-吡喃葡萄糖)-6,7,3′,4′-四羟基橙酮(4), 胡萝卜甙(5), 豆甾醇葡萄糖甙(6), 丁二酸(7)和 3-β-D-吡喃葡萄糖-1-羟基-6(反)-十四烯-8,10,12-三炔(8).

**关键词**　婆婆针，菊科，苯丙素甙

# CHEMICAL CONSTITUENTS OF BIDENS BIPINNATA

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**Abstract**　From the aerial parts of *Bidens bipinnata* Linn., three phenylpropanoid glucosides: i.e. 4-O-(6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (1), 4-O-(2″-O-acetyl-6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (2) and 4-O-(2″,4″-O-diacetyl-6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (3) were isolated. Among them, phenylpropanoid glucoside (3) was a new compound. Additionally, (Z)-6-O-(4″,6″-diacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone (4), 3β-gluco-β-sitosterol (5), 3β-gluco-stigmasterol (6), butanedioic acid (7)and 3β-D-glucopyranosyloxy-1-hydroxy-6(E)-tetradecene-8,10,12-triyne (8) were also obtained.

**Key words**　*Bidens bipinnata,* Compositae, Phenylpropanoid glucosides

*Bidens bipinnata* Linn., a weed of the Compositae family, is widely distributed in Yunnan Province (Wu *et al,* 1984). In traditional Chinese folk medicine, *B. bipinnata* Linn. has been used to cure sore throat, stomach disorder and jaundice(Den *et al,* 1993). The investigation of the chemical constituents of this plant led to the isolation and structure elucidation of one new phenylpropanoid glucoside 4-O-(2″,4″-O-diacetyl-6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (3) together with seven

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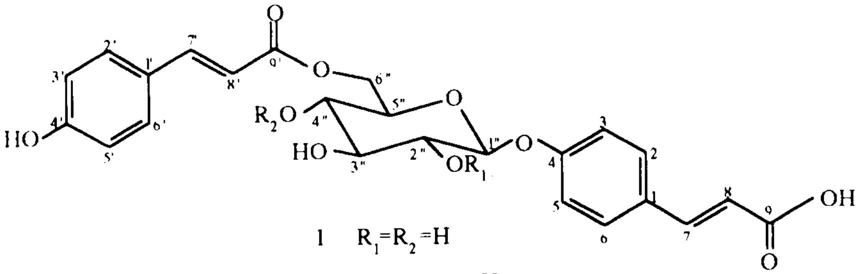
known compounds, 4-O-(6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (1)(Sashida *et al*, 1991), 4-O-(2″-O-acetyl-6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (2) (Sashida *et al*, 1991), (Z)-6-O-(4″,6″-diacetyl-β-D-glucopyranosyl)-6,7,3′,4′-tetrahydroxyaurone (4) (Rucker *et al*, 1994a), 3β-gluco-β-sitosterol (5), 3β-gluco-stigmasterol (6), butanedioic acid(7) and 3β-D-glucopyranosyloxy-1-hydroxy-6(E)-tetradecene-8,10,12-triyne (8) (Rucker etal, 1994b).

## RESULTS AND DISCUSSION

Compound 3 was obtained as white powders. The $^1H$ and $^{13}C$ NMR spectra of 3 showed that the structure possessed the same skeleton as compound 1 and two additional acetyl groups. This was confirmed by negative FAB mass (ion at m/z 555[M-H]⁻). The data of p-coumaroyl moiety agreed well with those of 1. The only difference between 3 and 1 was the sugar moiety. Two singlets at δ2.05 and 2.08 ppm in the $^1H$ NMR spectrum were coincident with two acetyl groups attached to the sugar moiety. The two signals ascribable to H-2″ and H-4″ markedly shifted downfield to δ 5.86 and 5.68 ppm, respectively. These facts revealed that the acetyl groups were linked to the C-2″-and C-4″-OH positions of the glucose. Thus, the structure of 3 was determined as 4-O-(2″,4″-O-diacetyl-6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid.



1 $R_1$=$R_2$=H

2 $R_1$=Ac, $R_2$=H

3 $R_1$=$R_2$=Ac

Since compound 1 and 2 were isolated from *B. bipinnata* by us and their spectral data were in good agreement with those of reported ones which were unambiguously identified on the basis of spectroscopic methods and chemical correlation, it is reasonable to think that C-6″-OH was acylated by p-coumaroyl moiety while C-2″-and C-4″ OH were attached to acetyl groups. But another possibility that the acetyl group was linked to C-6″-OH while p-coumaroyl moiety located at C-2″-or C-4″-OH still could not be absolutely excluded. The application of the long-rang heteronuclear correlation NMR experiment (COLOC) solved the problem. The observation that the signal of C-9′ showed long-rang couplings with H-6″, H-7′and H-8′ simultaneously indicated the p-coumaroyl moiety was indeed attached to C-6″-OH. Thus, compound 3 was unambiguously elucidated as 4-O-(2″,4″-O-diacetyl-6″-O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid.

Table 1 $^{13}C$ NMR data of 1-3 in $CD_3OD$

(400 M Hz, $\delta$ in ppm with reference to the signal of $CD_3OD$)

| | 1 | 2 | 3 |
|---|---|---|---|
| P-coumaroyl moiety | | | |
| 1,1′ | 129.5 | 130.1 | 130.1 |
| | 126.1 | 126.1 | 126.1 |
| 2,2′,6,6′ | 130.7 | 130.8 | 130.9 |
| | 130.1 | 130.1 | 130.2 |
| 3,3′,5,5′ | 117.6 | 117.6 | 117.7 |
| | 117.0 | 117.0 | 117.0 |
| 4,4′ | 161.7 | 161.7 | 161.8 |
| | 160.0 | 159.3 | 159.0 |
| 7,7′ | 145.5 | 145.5 | 146.0 |
| | 143.8 | 143.5 | 143.5 |
| 8,8′ | 118.9 | 119.4 | 119.5 |
| | 115.1 | 115.0 | 114.7 |
| 9,9′ | 169.4 | 169.4 | 169.3 |
| | 167.4 | 167.3 | 167.0 |
| Glucose moiety | | | |
| 1″ | 102.1 | 99.6 | 99.5 |
| 2″ | 74.9 | 74.8 | 74.6 |
| 3″ | 78.4 | 76.0 | 73.3 |
| 4″ | 71.6 | 71.6 | 72.2 |
| 5″ | 75.7 | 75.9 | 73.3 |
| 6″ | 64.5 | 64.1 | 63.0 |
| OAc | | 170.1 | 170.3 |
| | | | 170.0 |
| | | 21.0 | 20.9 |
| | | | 20.9 |

## EXPERIMENT

**General** All melting points were measured on a XRC-1 micro melting point apparatus produced by Sichuan University and uncorrected. Optical rotations were taken on a JASCO-20C digital polarimeter. IR spectra were recorded with a Perkin-Elmer 577 spectrometer. UV spectra were obtained on a UV 210A spectrometer. MS spectra were measured on a VG Autospec spectrometer. NMR spectra were run on a Bruker AM-400 spectrometer. The chemical shifts ($\delta$) were expressed in ppm with reference to the solvent signals. Coupling constants (J) were given in Hz.

**Plant material** The aerial parts of *Bidens bipinnata* Linn. were collected in Kunming, Yunnan, China, in July 20,1994. A voucher specimen is kept in the Herbarium of Kunming Institute of Botany.

**Extraction and isolation** The dried ground aerial parts of *Bidens bipinnata* Linn. (3.5kg) were extracted with ethanol ($4 \times 20$ L) at room temperature during four weeks to give crude extract (392 g), which was then partitioned with petroleum ether, ethyl acetate and n-butanol successively. The AcOEt part (110 g) was subjected to silica gel column (1.0 kg, 220-300 mesh) eluting with petroleum ether by increasing amount of ethyl acetate to afford six fractions.

After repeating silica gel and reversed phase silica gel as well as Sephadax LH-20 (eluent: $MeOH-H_2O$) column chromatography, eight compounds: 1(20 mg), 2(100 mg), 3(40 mg), 4(80 mg), 5(700

mg), 6(800 mg), 7(50 mg) and 8 (35 mg) were obtained.

**4-O-(6″ -O-p-Coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (1),** — $C_{24}H_{24}O_{10}$, White powders; EIMS (70 eV) m / z(%): 309 [M-coumaric acid]$^+$(4), 164[coumaric acid]$^+$(36), 147(56), 119(14), 107(19) and 79(100); $^{13}C$ and $^1H$ NMR data see Table 1 and 2 respectively.

**4-O-(2″ -O-Acetyl-6″ -O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (2)**—$C_{26}H_{26}O_{11}$, white powders; IR$\nu_{max}^{KBr}$cm$^{-1}$: 3480, 1702,1623, 1595, 1500, 1370, 1248, 1170, 1086, 1045 and 825; UV$\lambda_{max}^{MeOH}$nm(log ε):218.5, 223.0, 285.0, 293.0 and 304.0; EIMS (70 eV)m / z(%): 351[M-coumaric acid]$^+$(16), 164[coumaric acid]$^+$(57), 147(100), 119(22), 107(14), 91(25) and 79(15);FABMS (positive ion mode) m / z(%): 515[M+H]$^+$(2); $^{13}C$ and $^1H$ NMR data see Table 1 and 2 respectively.

Table 2 $^1H$ NMR data of 1-3 in $CD_3OD$

(400 M Hz, δ in ppm with reference to the signal of $CD_3OD$)

| | 1 | 2 | 3 |
|---|---|---|---|
| P-Coumaroyl moiety | | | |
| 2,2′ | 7.60(d,8.7) | 7.61(D,8.5) | 7.59(d,8.5) |
| 6,6′ | 7.56(d,8.6) | 7.57(d,8.5) | 7.58(d,8.5) |
| 3,3′ | 7.34(d,8.7) | 7.32(d,8.5) | 7.29(d,8.5) |
| 5,5′ | 7.21(d,8.6) | 7.21(d,8.5) | 7,20(d,8.5) |
| 7 | 7.98(d,15.9) | 7.94(d,15.9) | 7.96(d,16.0) |
| 7′ | 7.92(d,15.9) | 7.91(d,15.9) | 7.95(d,16.0) |
| 8 | 6.75(d,15.9) | 6.78(d,15.8) | 6.75(d,16.0) |
| 8′ | 6.63(d,15.9) | 6.63(d,15.8) | 6.64(d,16.0) |
| Glucose moiety | | | |
| 1″ | 5.66(d,7.2) | 5.69(d,8.1) | 5.68(m,overlap) |
| 2″ | 4.24(dd,7.2,9.3) | 5.87(dd,8.1,9.0) | 5.86(dd,7.7,9.4) |
| 3″ | 4.35(m,overlap) | 4.40(dd,9.0,9.0) | 4.48(dd,9.4,9.4) |
| 4″ | 4.35(m,overlap) | 4.23(dd,9.0,9.3) | 5.68(m,overlap) |
| 5″ | 4.35(m,overlap) | 4.34(m) | 4.40(m) |
| 6″a | 5.17(dd,3.2,11.8) | 5.13(dd,3.4,11.8) | 4.74(dd,2.4,12.0) |
| 6″b | 4.92(dd,6.6,11.8) | 4.89(dd,6.2,11.8) | 4.67(dd,5.9,12.0) |
| OAc | | 2.08(s) | 2.08(s) |
| | | | 2.05(s) |

**4-O-(2″ ,4″ -O-Diacetyl-6″ -O-p-coumaroyl-β-glucopyranosyl)-p-coumaric acid (3)**—$C_{28}G_{28}O_{12}$, white powders, mp: 192~194℃, $[\alpha]_D^{25}$-60.1° ($C_5D_5N$, c 0.362); IR$\nu_{max}^{KBr}$cm$^{-1}$:3440, 1735, 1722, 1700, 1642, 1618, 1520, 1390, 1250, 1190, 1078, 994 and 848; UV$\lambda_{max}^{MeOH}$nm (log ε): 216.5(4.38), 284.0(4.53), 289.0(4.52, sh) and 305.0(4.46, sh); EIMS(70 eV)m / z(%): 393[M-coumaric acid]$^+$(8), 164[coumaric acid]$^+$(44), 147(100), 119(19), 107(9), 91(21) and 65 (16); FABMS(negative ion mode):555[M-H]$^-$(100); HR FABMS (negative ion mode) m / z: 556.1632 (calc. 556.1581); $^{13}C$ and $^1H$ NMR data see Table 1 and 2 respectively.

**(Z)-6-O-(4″ ,6″ -Diacetyl-β-D-glucopyranosyl)-6,7,3′ ,4′ -tetrahydroxyaurone (4)**—$C_{25}H_{24}O_{13}$, orange crystals (MeOH-$H_2O$), mp: 195~197℃; IR$\nu_{max}^{KBr}$cm$^{-1}$: 3220-3360(br.), 1725, 1685, 1835, 1590, 1504, 1360,1270, 1168, 1085 and 1035; UV$\lambda_{max}^{MeOH}$nm(log ε): 238.5(4.06, sh), 272.0(4.01), 328.0(4.11), 417.0(4.38); +NaOMe:264.0,285.0(sh), 348.5, 493,0; +$AlCl_3$:250.0(sh), 292, 5, 321.0, 456.5; +$AlCl_3$+HCl: 242.0(sh), 277.5, 323.5, 415.0;+NaOAc:263.5, 358.0, 482.5; +NaOAc+$H_3BO_3$: 284.5, 327.5, 443.0;EIMS (70 eV)

m / z(%): L286[aglycone]$^+$(100), 258[agl−CO]$^+$(4), 229[acetyglucosyl−$H_2O$]$^+$(14), 169(16), 153(43), 152(62), 127(26),115(21), FABMS (positive ion mode) m / z(%): 533[M+H]$^+$(7) and 287[agl+H]$^+$(16).

**3$\beta$−Gluco−$\beta$−sitosterol (5)**—$C_{35}H_{60}O_6$, white powders; EIMS (70 eV) m / z(%): 414, 396, 382, 329, 255, 213, 145 and 81; $^1$H NMR (pyridine−$d_5$) $\delta$:3.96(1H, m, H−3), 5.34(1H, br.s, H−6), 0.65−1.02(18H, m, 6×$CH_3$), 5.05(1H, d, J=7.6, Hz, H−1′), 4.05(1H, dd, J−7.6, 9.0 Hz, H−2′), 4.29(1H, m, H−3′), 4.29(1H, m, H−4′), 3.96(1H, m, H−5′), 4.41(1H, dd, J=5.2, 11.8 Hz H−6′ b) and 4.58(1H, d, J=11.8 Hz H−6′ a).

**3$\beta$−Gluco−stigmasterol (6)**—$C_{35}H_{58}O_6$, white powders; EIMS (70 eV) m / z(%): 412, 397, 369, 312, 300, 269, 253, 133, 109, 95, 81, 69 and 55; $^1$H NMR (pyridine−$d_5$) $\delta$: 3.96(1H, m, H−3), 5.34(1H, br.s, H−6), 5.20(1H, dd, J=8.6, 15.0 Hz, H−22), 5.05(1H, m, H−23), 0.66−1.02(18H, m, 6×$CH_3$),5.05(1H, m, H−1′), 4.05(1H,dd, J=7.6, 8.8 Hz H−2′), 4.28(1H, m, H−3′), 4.28(1H, m, H−4′), 3.96(1H, m, H−5′), 4.41(1H, dd, J=5.2, 11.7 Hz H−6′ b) and 4.56(1H, d, J=11.7 Hz H−6′ a).

**Butanedioic acid (7)**— $C_4H_6O_4$, colorless crystals (from MeOH), mp: 167∼ 170℃ ; IR$\nu_{max}^{KBr}cm^{-1}$: 3300−2500(br.), 1690(br.), 1405,1300, 1193, 910, 795 and 630; EIMS (70eV) m / z(%): 119[M+H]$^+$(17),100(61), 74(78) and 55(100); $^{13}$C NMR (pyridine−$d_5$) $\delta$: 175.3(C−1) and 30.4(C−2); $^1$H NMR $\delta$: 12.59(1H,br.s,OH) and 3.00 (each 2H,s,2×$CH_2$).

**3$\beta$−D−Glucopyranosyloxy−1−hydroxy−6(E)−tetradecene−8,10,12−triyne (8)**— $C_{20}H_{26}O_7$, brown pwoders; IR$\nu_{max}^{KBr}cm^{-1}$: 3340, 2895, 2200, 1605, 1413, 1360, 1158, 1070 and 1010; UV$\lambda_{max}^{MeOH}$nm: 231.0,233.5(sh), 240.0, 257.5, 272.0, 288.5, 308.0 and 329.0; EIMS (70 eV) m / z(%): 216[aglycone]$^+$(65), 198(46), 165(49), 153(70), 141(55), 127(100), 115(70), 101(54),85(57), 77(47), 73(95) and 60(78); FABMS (positive ion mode) m / z: 379[M+H]$^+$; $^{13}$C NMR (pyridine−$d_5$) $\delta$: 58.4(C−1), 39.5(C−2), 78.8(C−3), 349(C−4), 29.5(C−5), 152.0(C−6), 108.2(C−7), 60.1(C−8)*, 65.4(C−9)*, 67.4(C−10)*, 73.8(C−11)*, 76.0(C−12)*, 79.4(C−13)*, 4.1(C−14), 104.6(C−1′),75.4(C−2′),78.2(C−3′), 72.5(C−4′), 76.6(C−5′) and 63.5(C−6′); $^1$H NMR (pyridine−$d_5$) $\delta$: 1.93(2H,m,$H_2$−2), 1.68(2H,m,$H_2$−4), 2.38 and 2.52(each 1H, m, H−5),6.41(1H, dt, J=7.0, 16.0 Hz, H−6), 5.62(1H, d, J−16.0 Hz H−7), 4.86(1H, d, J=7.8 Hz, H−1′) and 4.60(1H, dd, J=2.2,11.4 Hz H−6′ a).

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